PATENT SPECIFICATION (11) 1342974

1342974

(21) Application No. 42626/71 (22) Filed 13 Sept. 1971

(44) Complete Specification published 9 Jan. 1974

(51) International Classification A23L 1/30 A21D 2/00 2/02 2/14

(52) Index at acceptance

A2B 1B 1C 1G

(72) Inventors LEWIS DAVID MORSE and PAUL ALOYSIUS HAMMES

(19)

(54) FOOD COMPOSITIONS

(71) We, MERCK & CO INC, a corporation duly organised and existing under the laws of the State of New Jersey, United States of America, of Rahway, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to edible preparations containing lipoid material, particularly processel cereal grains, including related baked products such as bread, rolls, buns, cereals. cakes, biscuits or other baked desserts or snack food. This invention provides an edible preparation containing lipoid material subject to rancidity and an enriching nutritionally available iron source in particulate form, in which the iron-containing particles are encapsulated in a coating to overcome the effect of the iron on the lipoid material.

The microencapsulation of metabolically available iron compounds is particularly valuable for use in baked products such as breads and cereals. An especial inherent advantage of this is that the iron is shielded by the coating thereon from exerting an effect on other ingredients in products derived from processed cereal grains; such ingredients may be those that occur naturally in the cereal grain or that are added anywhere during processing from grain to final consumer item.

Iron compounds, for example ferrous sulphate, exert catalytic effects on the oxidation of the fats that are always present in processed cereal grain. This catalytic action tends to induce rapid rancidity of the fats. Also, iron compounds tend to modify the rheology of dough, and thereby alter the appearance of the consumer item. The use of microencansulated iron in accordance with this invention is intended to overcome both of these influences of iron upon foods derived from cereal grains.

As iron is an essential nutritional substance, there are, in the U.S.A., State and Federal regulations governing its use in baked goods, as nearly everyone consumes such food every day. A deficiency of iron causes a hypocromic anaemia and a daily consumption of less than 10 milligrams may cause morphological changes such as hypochromic, microcytic, anisocytosis and poikilocytosis. The most apparent subjective symptoms of an iron deficiency are generalised weakness, fatigability and irritability.

In view of this metabolic need for iron it is apparent that its daily consumption in processed cereal grains affords an opportune manner of satisfying this nutritional need. The use of microencapsulated iron as is taught by this invention overcomes the effects that iron has on processed cereal foods. Moreover, the coating on the iron shields its bad taste from the consumer, but after it has been consumed the iron becomes available in the body.

The microencapsulation of the iron compound involves the known arts of polymer/polymer incompatibility, coacervation, and film formation from polymer solutions by loss of solvent. Representative of this prior art are the British patent 1,016,839, and the U.S. patents 3,106,308, 3,155,590, 3,495,988, and 2,800,457. Other microencapsulation processes which may be used are disclosed in Netherlands patent 6,611,661 and in French patent 1,453,745. The present invention involves the adaptation of those processes and the resulting products to the problem of microencapsulating iron compounds.

The invention contemplates both water-insoluble coatings and water-soluble coatings. The water-insoluble coating is permeable due to its thinness and consequently gastric fluids pass through it. This leaches out the contained iron salt so that it is available for nutrition of the host. The water-soluble coating dissolves in gastric juices and thereby releases the iron compound.

A suitable water insoluble coating is ethylcellulose and a suitable solvent for it is cyclohexane. The ethylcellulose should preferably have a 47.5% ethoxyl content and a 100 cps. viscosity but a range of 45.0—50%

ethoxyl content and a 95—10 100 cps. viscosity is permissible. The viscosity is measured as known in the art, at 25°C. as a 5% by weight solution in an 80:20 toluene-ethanol mixture. On the basis of 100 grams of cyclohexane there can be added 1 to 5 grams, preferably 2 grams, of the ethylcellulose to vary the time of release of the iron compound. Other suitable coatings materials are hydroxypropylmethyl cellulose, hydroxyethyl cellulose and ethylhydroxyethyl cellulose.

When ethylcellulose is used, the phase separation inducing agent is polyethylene and the material should preferably have a molecular weight of from 5000 to 10,000 (an average of 700 is preferred) and from 1 to 5 grams, preferably 2 grams, of it should be added per 100 grams of the cyclohexane. The invention, however, involves the elimination of a phase separation inducing agent and the use only of the coating agent is taught in the above mentioned Netherlands patent 6,611,661.

The invention also includes microencapsulation of the iron in a geltain-gum arabic-water system using the techniques for instance of the aforementioned U.S. patent 3,495,988. Other coating agents are like polymers having hydroxyl and carboxyl groups.

The preferred iron compound is ferrous fumarate, but the invention can be practiced with the use of the citrate, gluconate, lactate or sulphate salt. These salts are generally used for enrichment of flour mixes and in pharmaceutical forms such as chewable multivitamin tablets ordinary swallowable tablets, capsules and liquid pharmacutical preparations. Elemental or reduced iron may also be used. Ferric compounds which may be used are: ferric chloride, ferric phosphate and ferric ammonium citrate. The invention contemplates the use of any metabolically available iron compound.

The iron compound preferably is of the size to pass through a U.S. No. 100 gauge sieve but this is by no means essential as the iron compound particles may range from as large as a 20 gauge sieve size down to as small as to pass through a 325 gauge sieve. It may be added over a wide range, namely from 2 to 120 grams based on 100 grams of cyclohexane.

The following examples are representative of a water in soluble coating.

EXAMPLE 1

The following were dispersed in 300 gm. cyclohexane, using an upthrust turbine impeller:

6 gm. Ethylcellulose (47.5% ethoxy content by weight; viscosity 100 cps. as measured above).

6 Gm. Polyethylene granules (molecular weight about 7000).

110 gm. Ferrous fumarate, sized to pass through a 320 gauge sieve.

The system was stirred with heating. At 20°C both the ethylcellulose and the polyethylene had dissolved in the cyclohexane.

Stirring was continued while the system was allowed to cool. As the temperature dropped, solvated ethylcellulose developed as a separate phase due to the presence of the polyethylene. This is a known art, described in the literature as an example of coacervation resulting from polymer/polymer incompatibility. The solvated polyethylene distributed in the cyclohexane as droplets by the turbine, tended to wet the ferrous fumarate particles and to envelop then. As the temperature dropped further, the ethylcellulose lost solvent and developed into solid encapsulating walls. The continuous phase, cyclohexane, contained minute particles of polyethylene. At 45°C the walls had stopped building up. Cold cyclohexane was added to reduce the temperature still further. The supernatant cyclohexane was poured off together with the minute particles of polyethylene. The microcapsules were resuspended in clean cyclohexane. This was continued until the capsules were washed clean of polyethylene and other debris. The capsules were spread to dry.

The resultant capsules, with a theoretical 95% ferrous fumarate content, when screened through standard Taylor sieve, were 7% +60 mesh, and 93% −60 mesh.

To demonstrate nutritional availability of the ferrous fumarate, 0.50 gm. capsules were put into 200 ml. simulated gastic fluid at 98.7°F, and held in a shaking temperature controlled water bath. All of the internal phase was found to have been released from the capsules in five minutes.

EXAMPLE 2

Example 1 is carried out but in each case the ethylcellulose is within the range of 3 to 15 gms. Thicker walls are formed by increasing the ethylcellulose weight up to 15 gm.

EXAMPLE 3

To provide a more economical process Example 1 is carried out but only 3 gm. polyethylene granules were used. This will be sufficient to phase out the ethylcellulose. Also, only 45 gm. ferrous fumarate is used.

EXAMPLE 4

Another way to prepare very thick capsule walls is to follow Example 1, but use only 6 gm. of the iron salt.

EXAMPLE 5

Instead of using ferrous fumarate any one of the above mentioned iron salts is used in an equal amount. Or, metallic or reduced iron may be used in a finely divided form.

EXAMPLE 6

The processes of Examples 1 to 5 are carried out but the selected iron salt is mostly of a larger 20 gauge sieve size. Any in-between size down to as as small as a 320 U.S. gauge size may be used.

The following examples forms a water-soluble coating. The gelatin in the coating wall is hydrolysed to a substantial extent so that the iron compound is released.

EXAMPLE 7

An 11% solution of 250 Bloom porskin gelatin in distilled water was prepared (I) and held at 55°C. An 11% solution of gum Arabic in distilled water was prepared (II) and held at 55°C. A 2% solution of ethylene maleic anhydride copolymer (Visc. 2.0 cps. before pH adjustment), adjusted with sodium hydroxide to pH 9 was prepared (III). A 2% solution of ethylene maleic anhydride copolymer (Visc. 7.0 cps before pH adjustment) adjusted with sodium hydroxide to pH 9 was prepared (IV).

90 ml. of (I), 90 ml. of (II), 20 ml each of (III) and (IV), were blended with 500 ml. distilled water (previously warmed to 55°C), and kept stirring with an upthrust turbine impellor. The pH of the system was 7.0. Microscopic examination showed a rich dispersion of coacervate droplets of gelatin/gum Arabic/ethylene maleic anhydride copolymer in water. The dispersion of the highly hydrated colloidal complex was kept stirring, and allowed to cool to 35°C to ±4.5°C. At that temperature 72 gm. ferrous fumarate was added. Microscopic examination showed that coacervate droplets were wetting small aggregates of ferrous fumarate particles. The coecervate droplets fused together to form a hydrated film. As the temperature dropped to 25°C. wall build-up continued. At 25°C there were discrete microcapsules of aggregated ferrous fumarate particles. The system was chilled to 10°C. Some of the slurry (V) was removed for later treatment. To the rest of the slurry (VI), 430 ml. was added 2.0 ml. of 25% aqueous glutaraldehyde to crosslink the capsular wall material. System (VI) was allowed to stir overnight. Capsules of slurry (V) and (VI) were washed with chilled distilled water, dehydrated by washing with anhydrous ethanol, and then air dried.

The crosslinked capsules, screened through Taylor sieves, had the following size distribution:

	% by weight
+60 mesh	0.6
−60/+100	1.5
−100/+200	40.0
−200/+270	41.9
−270/+325	8.2
−325	7.3

0.25 gm. of the −325 mesh fraction was dispersed in 200 ml. simulated gastric fluid at 37°C. in a shaking, temperature controlled bath. All of the iron was released in five minutes.

To test the product of Example 7, three screw-cap glass vials, 2 fl. oz. capacity were filled to one-quarter inch from the top with a solution of distilled water containing 0.338 mg./ml. ascorbic acid and 3.25 mg./ml. citric acid.

The vials were treated further as follows:

Vial I.
Add 0.309 mg/ml. ferrous fumarate. Cap, and seal with paraffin.

Vial II.
Add 0.385 mg./ml. microcapsules of Example 7, the −325 fraction, not crosslinked. Cap, and seal with paraffin.

Vial III:
Add 0.385 mg./ml. microcapcules of Examples 7, the −325 fraction, crosslinked. Cap, and seal with paraffin.

The vials were opened 35 days later and the contents analysed for ascorbic acid. The results were as follows:

	Vial I	Vial II	Vial III
Ascorbic Acid (mg./ml.)	0.0097	0.05	0.0658

EXAMPLE 8

Ferrous Sulphate is blended into wheat flour at from 13 mg. to 75 mg. iron per pound of flour to form System I.

Microencapsulated ferrous sulphate, prepared as in Example 1, is included in wheat flour at from 13 mg. to 75 mg. iron per pound of flour to form System II.

Systems I and II are stored in typical flour bags at various temperatures and humidities to simulate usual storage conditions.

Upon examination at 3 months' storage, System I is rancid. System II is not. The microcapsule wall has prevented the iron from catalysing the oxidation of lipoid material. Also, the iron is taste masked.

The microencapsulated iron compound can be added to any other processed cereal grain.

EXAMPLE 9

Example 8 is followed but with any other iron salt of biological significance.

EXAMPLE 10

Example 8 is followed but with an iron salt which is insoluble in water and using the encapsulation technique of Example 7.

EXAMPLE 11

The wheat flour or other processed cereal grain of Examples 8, 9 and 10 is weighted out so that 8 mg. to 50 mg. of iron are added per pound of bread.

EXAMPLE 12

Example 11 is followed but with cold breakfast cereal, flakes, puffer, or extruded.

EXAMPLE 13

Example 11 is followed but with hot breakfast cereals.

EXAMPLE 14

Example 11 is followed but with snack food items, processed from edibles comprised of protein and/or carbohydrat and fat substances that are formed and heat treated.

EXAMPLE 15

Example 11 is followed but with crackers.

EXAMPLE 16

Example 11 is followed but with frozen dough preparations and refrigerated dough preparations.

EXAMPLE 17

Example 11 is followed but with refrigerated and frozen baked items.

EXAMPLE 18

Example 11 is followed but with cakes, rolls or pastries.

EXAMPLE 19

Example 11 is followed with the preparation of the following products: doughnuts, sandwich creams, peanut butter cracker sandwiches, biscuits, wafers, tea biscuits, confections, chocolate enrobed cereal products, pies, muffins, English muffins, pop-ups, and turnovers.

EXAMPLE 20

Instead of the baked products of Examples 14 to 19, the dry packaged mixes for making them are to contain the microencapsulated iron.

EXAMPLE 21

The encapsulated iron may be added to syrups, fillings, toppings and like adjuncts ordinarily applied to bakery products.

EXAMPLE 22

Capsules were prepared sucessfully as in Example 1 but no polyethylene was used. The ethylcellulose phased out without the polyethylene as in Netherland Patent 6,611,661. These capsules may be used in any of the products mentioned above.

EXAMPLE 23

Capsules were prepared successfully as in Example 22, but the ethylcellulose used had a viscosity of 45 cps, rather than 100 cps.

EXAMPLE 24

Microcapsules were prepared according to the French Patent No. 1,453,745.

Thus, to 400 gm. 1% aqueous hydropropylmethylcellulose was added 50 gm. finely divided reduced iron (metallic iron), with stirring. 400 Ml. 25% dextran solution was added slowly with stirring. This phased out the hydroxypropyl methylcellulose. The system was heated at 60°C for ½ hour to harden the capsule walls. 7.5 gm. 25% aqueous tannic acid was added to crosslink the capsule walls and thereby strengthen them. The system was stirred for 2 hours. The capsules were washed with cold water and spread to dry and then used in any of the above bakery or related products.

EXAMPLE 25

This utilizes the general process of U.S. patent 3,016,308. Fifty grams of finely divided reduced iron (metallic iron) is dispersed in 700 gm. 10% aqueous hydroxyethylcellulose (300 cps. at 20°C as a 5% aqueous solution). The dispersion was spray dried at 245°F to yield microcapsules to be used as above.

EXAMPLE 26

Finely divided reduced iron was microencapsulated using the process taught in U.S. Patent 3,495,988.

A 36% solution of gelatin was brought to 40°C. with stirring. 50 g. finely divided reduced iron was added with stirring, keeping the temperature of the system at 40°C. to form System I.

System I was added with stirring to 600 gm. white mineral oil. The white mineral oil was at 30°C. The resultant System II was a slurry of gel in mineral oil, the gel entraining the iron particles. The slurry particle size was about 100 μ.

System II was poured with stirring into 3 liters 95% ethanol previously adjusted to 20° C. The system II was allowed to stir for an hour to allow dehydration of the spheres Liquid was decanted. The spheres were washed with 95% aqueous ethanol at 20°C and spread to dry. They are used in making any of the bakery or like products mentioned above.

EXAMPLE 27

The process of Example 26 was used using gum Arabic entraining material.

33.3 gm. finely divided reduced iron was added with stirring to 200 gm. 50% aqueous gum Arabic at 10°C. to yield System I.

System I was added to a mixture of 500 gm. castor oil and 250 gm. ethanol at 10°C, with stirring to yield a slurry of 100 μ spheres in the liquid, constituting System II.

System II was added to 2 liters anhydrous ethanol at 10°C. with stirring. Stirring was continued to allow for dehydration of the spheres.

The spheres were drained of liquid, washed with ethanol and spread to dry. They are used as above described.

EXAMPLE 28

Spheres were prepared as in Example 27, using however 25% aqueous poly (methyl vinyl ether (maleic anhydride) specific viscosity 0.1—0.5, in place of the 50% aqueous gum Arabic.

EXAMPLE 29

Spheres were prepared as in Example 27, but using gum carrageenan in place of the gum Arabic. The resultant spheres are used as above described.

EXAMPLE 30

Spheres were prepared as in Example 27, using poly (ethylene maleic anhydride) [low molecular weight) in place of the gum Arabic. The resultant spheres are used as above described.

EXAMPLE 31

Example 27 is followed with Algin in place of gum Arabic.

EXAMPLE 32

Example 27 is followed with gum Guar in place of gum Arabic.

EXAMPLE 33

Example 27 is followed with locust bean gum in place of gum Arabic.

EXAMPLE 34

Example 27 is followed with yellow dextrin in place of gum Arabic.

EXAMPLE 35

Example 27 is followed with dextrin in place of gum Arabic.

EXAMPLE 36

Example 27 is followed with poly (acrylic acid) in place of gum Arabic.

WHAT WE CLAIM IS:—

1. An edible preparation containing lipoid material subject to rancidity and an enriching nutritionally available iron source in particulate form, in which the iron-containing particles are encapsulated in a coating to overcome the effect of iron on the lipoid material.

2. A preparation according to Claim 1 that is a processed cereal grain.

3. A preparation according to Claim 1 that is a bakery product.

4. A preparation according to Claim 1 that is an adjunct to be applied to a bakery product.

5. A preparation according to any one of Claims 1—4, in which the microencapsulating coating is a water-insoluble polymer.

6. A preparation according to any one of Claims 1—4 in which the microencapsulating coating is a water-soluble polymer.

7. A premix composition containing lipoid material subject to rancidity and an enriching nutritionally available iron source in particulate form, in which the iron particles are encapsulated in a coating to overcome the effect of the iron on the lipoid material.

8. A premix composition according to Claim 7 in which the iron source is metallic iron.

9. A premix composition according to Claim 7 in which the iron is in a biologically available salt.

10. A method of adding enriching nutritionally available iron to an edible preparation containing lipoid material that would be affected by the iron, which comprises separately encapsulating the iron to overcome its effect on said lipoid material and then adding the encapsulated iron to its preparation.

11. A method according to Claim 10 in which the microencapsulation includes the steps of stirring a mixture of water, gelatin, gum Arabic and ethylene maleic anhydride copolymer at a pH 7.0 at 55°C, allowing it to cool to 35°C±0.5°C while still being stirred, and then adding ferrous fumerate.

12. A method of making a preparation according to Claim 1 substantially as hereinbefore described in any one of the foregoing Examples.

13. A preparation according to Claim 1, when prepared by a method as claimed in Claim 10, 11 or 12.

For the Applicants,
D. YOUNG & CO.,
Chartered Patent Agents,
9 & 10, Staple Inn,
London, WC1V 7RD.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1974.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.